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⑮ 発明の名称 高強度リン酸カルシウム焼結体の製造方法

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明細書

1. 発明の名称

高強度リン酸カルシウム焼結体の製造方法

2. 特許請求の範囲

カルシウム/リン原子比 14~175 のカルシウムのリン酸塩を主体とする粉末に、焼成後のリン酸カルシウム焼結体に対し 0.5~15 重量% のアルカリ金属、亜鉛および/またはアルカリ土類金属の酸化物-リン酸系フリットを添加して焼成する方法において、前記粉末の比表面積が 20~80 μ^2/g であり、該フリットの比表面積と前記粉末との比が 1/10~1/1 であることを特徴とする高強度リン酸カルシウム焼結体の製造方法。

3. 発明の詳細な説明

本発明は、普通焼結により高強度のリン酸カルシウム焼結体を製造する方法に関するものである。

リン酸カルシウムは生体と親和性を有し、その焼結体は骨、歯に代わり得る生体材料として

用いることが提案されている。その他、その高緻密特性を利用し I C パッケージ基板として用いる外、高膨張性のセラミック材料としても有用である。

従来このリン酸カルシウム焼結体の製造方法としては、プレス後常圧で焼結する普通焼結法、ホットプレス法等がある。リン酸カルシウム粉末を単味で常圧下に焼結(普通焼結)させたとき、圧縮強度 900 kg/cm² 程度(セラミックス 10 [7] 1975. 474 頁)で緻密度が低くまた、焼成後の冷却過程においてスポーリングを発生し易く即ちスポーリング抵抗に弱いという欠点がある。

他方、ホットプレス法では圧縮強度 1000~2000 kg/cm²(医用器材研報 [Reports of the Institute for Medical & Dental Engineering] 7 卷 113~118 頁 (1973)) と強度はかなり高くなるが、製法が複雑であり、装置コストが大であって量産も困難であるという欠点があった。

本願出願人は、上記従来技術の欠点を除去するものとして、カルシウム/リン原子比 14~

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175のカルシウムのリン酸塩を主体とする粉末に、焼成後のリン酸カルシウム焼結体に対し0.5~15重量%のアルカリ金属、亜鉛および/またはアルカリ土類金属の酸化物-リン酸系フリットを含有せしめ焼結する方法を特開昭55-140756号公報において開示した。発明者等は鋭意研究の結果、上記公報に開示した方法のうち、カルシウムのリン酸塩を主体とする粉末に比表面積20~80m²/gのものを使用し、フリットにその比表面積が該粉末の比表面積以上で該粉末の比表面積の3倍以下のものを使用するのが望ましいことを見出した。

本発明は上記の知見にもとづいてなされたもので、その要旨は特許請求の範囲に記載の通りである。以下本発明で使用する原料の比表面積を上記のように限定した理由を説明する。

カルシウムのリン酸塩を主体とする粉末の比表面積が20m²/gに満たないと緻密で高強度の焼結体が得られず、80m²/gを超えると超微粉となり取扱い困難のため20~80m²/gに限定し

た。

フリットの比表面積がカルシウムのリン酸塩を主体とする粉末のそれより小さいとフリットが均一に分散せず焼結体の強度が低下し、他方該粉末の比表面積の3倍を超えると超微粉となり凝集したり、水和層が生じたりして逆に焼結体内部の空孔が多くなり強度が低下するので上記のように限定した。

以下実施例を示す。

実施例

第1表に示す組成となるようH₃PO₄, BaCO₃, CaCO₃およびAl₂O₃を秤量混合し、混合物をアルミナ坩堝に入れて大気中第1表に示す温度で溶融し、溶融物をカーボン板上に流し、放冷してフリットAおよびフリットBを得た。フリットA, Bの特性値も第1表に併記する。

第 1 表

フリットの種類	組成(モル%)			
	P ₂ O ₅	BaO	CaO	Al ₂ O ₃
A	46	32	20	2
B	47	3	49	1

表

第 2 表

焼結体 番号	粉末 種類	含有量 (wt%)	比表面積 (m ² /g)	抗折強度 (kg/cm)	備考	
					抗折強度範囲外	抗折強度範囲内
1	水酸アバタイト	100	-	0	800	抗折強度範囲外
2	"	95	A	0.6	5	1450
3	"	95	A	25	5	2080
4	"	95	A	45	5	2340
5	"	95	B	0.6	5	1200
6	"	95	B	25	5	1810
7	"	95	B	45	5	2000
8	第三リン酸カルシウム	95	A	25	5	1750
9	混合物	95	A	25	5	1670

注) 焼結体No.1は、特にスポーツリング抵抗が弱かつた。

Date: September 7, 2005

Declaration

I, Michihiko Matsuba, President of Fukuyama Sangyo Honyaku Center, Ltd., of 16-3, 2-chome, Nogami-cho, Fukuyama, Japan, do solemnly and sincerely declare that I understand well both the Japanese and English languages and that the attached document in English is a full and faithful translation of the copy of Japanese Unexamined Patent No. Sho-60-161368 laid open on August 23, 1985.



Michihiko Matsuba

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METHOD FOR PRODUCING HIGH-STRENGTH CALCIUM PHOSPHATE SINTERED
COMPACT

Japanese Unexamined Patent No. Sho-60-161368

Laid-open on: August 23, 1985

Application No. Sho-59-18043

Filed on: February 2, 1984

Inventor: Kazuo KONDO, et al.

Applicant: NGK Spark Plug Co., Ltd.

SPECIFICATION

1. TITLE OF THE INVENTION

METHOD FOR PRODUCING HIGH-STRENGTH CALCIUM PHOSPHATE SINTERED
COMPACT

2. WHAT IS CLAIMED IS:

A method for producing a high-strength calcium phosphate sintered compact in which a powder mainly composed of calcium phosphate with a calcium/phosphorus atomic ratio of 1.4 through 1.75 is added with an alkali metal, zinc, and/or alkaline earth metal oxide - phosphate frit by 0.5 through 15% by weight and the powder is sintered, wherein the specific surface area of the powder is 2.0 through 8.0 m²/g, and the ratio of the specific surface area of the frit and the specific surface area of the

powder is 1/1 through 3/1.

3. DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a method for producing a high-strength calcium phosphate sintered compact by normal sintering.

Calcium phosphate has affinity with a living body and it has been proposed that a sintered compact thereof is used as a living body material that can be used in place of a bone or tooth. In addition, by using its high compactness, calcium phosphate is useful as an IC package substrate and a ceramic material with high expansibility as well.

Conventionally, as a method for producing this calcium phosphate sintered compact, a normal sintering method in that sintering is performed at normal pressures after pressing, and a hot press method, etc., are used. When a calcium phosphate powder is singly sintered (normally sintered) at normal pressures, its compactness is low as a compression strength of approximately 900 kg/cm^3 (Ceramics 10[7] 1975, pp. 474), spalling easily occurs in the cooling process after sintering, that is, the compact is low in spalling resistance.

On the other hand, in the hot press method, the strength becomes much higher as a compression strength of 1000 through 2000 kg/cm^2 (Reports of the Institute for Medical & Dental

Engineering, Vol. 7, pp. 113 through 118 (1973)), however, its producing method is complicated, and the costs for the facilities are high, and mass production is difficult.

To eliminate the defects of the conventional techniques, the present applicant disclosed, in Japanese Unexamined Patent Publication No. 55-140756, a method for sintering by containing an alkali metal, zinc, and/or an alkaline earth metal oxide - phosphate-based frit by 0.5 through 15% by weight in the calcium phosphate sintered compact after being sintered of the powder mainly composed of calcium phosphate with a calcium/phosphorus atomic ratio of 1.4 through 1.75. The inventors earnestly studied, and as a result, they found that, among the methods disclosed in the above-described publications, desirably, the method in which a powder with a specific surface area of 2.0 through 8.0 m²/g was used as a powder mainly composed of calcium phosphate, and a frit that has a specific surface area being larger than that of the powder and three times or more the specific surface area of the powder area was preferable.

The present invention was made in view of the above-described circumstances, and the gist thereof is as described in the claim. Hereinafter, reasons for limitation on the specific surface area of the raw material used in the invention are described

below.

Unless the specific surface area of a powder mainly composed of calcium phosphate is less than $20 \text{ m}^2/\text{g}$, a sintered compact that is compact and highly strong cannot be obtained, and if $80 \text{ m}^2/\text{g}$ is exceeded, the powder becomes ultrafine and its handling becomes difficult, so that the range is limited to 2.0 through $8.0 \text{ m}^2/\text{g}$.

If the specific surface area of the frit is smaller than that of the powder mainly composed of calcium phosphate, the frit does not evenly disperse and the strength of the sintered compact lowers, and on the other hand, if the specific surface area exceeds three times of the specific surface area of the powder, the powder becomes ultrafine and aggregates, a hydrated layer is formed, the air holes inside the sintered compact increase and the strength lowers to the contrary. Therefore, the above-described limitation is set.

An example is shown below.

Example

H_3PO_4 , BaCO_3 , CaCO_3 , and Al_2O_3 were measured and mixed so as to obtain the compositions shown in Table 1, and the mixtures were put into an alumina crucible and melted at the temperatures shown in Table 1 in the atmosphere, and the melts were poured on a carbon plate and left and cooled, whereby frit A and frit

B were obtained. Characteristic values of the frit A and frit B are also shown in Table 1.

Table 1

Frit type	Composition (% by mole)			
	P ₂ O ₅	BaO	CaO	Al ₂ O ₃
A	46	32	20	2
B	47	3	49	1

The frits were crushed at alternate times in an alumina ball mill and three types with specific surface areas of 0.6, 2.5, and 4.5 m²/g of the respective frits A and B were prepared.

The above-described frits with different specific surface areas, apatite hydroxide with a specific surface area of 2.4 m²/g, calcium triphosphate with a specific surface area of 2.4 m²/g, and a mixture of these (a mixing ratio: 1/1) were wet-mixed at proportions shown in Table 2, and as a binder, three parts by weight of camphor were melted in ether and added to 100 parts by weight of an all-inorganic powder, and after drying, the mixtures were formed at a pressure of 800 kg/cm² into a size of 12mm in width × 40mm in length × 4mm in thickness, and then sintered under conditions in that the temperature rising rate was 300°C/hr and respective holding times at the temperature stages from 1000 through 1500°C were one hour, whereby sintered compacts were produced. Among the sintered compacts sintered at the respective temperatures, deflecting strengths were

measured and the highest strength is shown as an optimal example in Table 2.

Table 2

Sintered compact No.	Powder		Frit			Deflecting strength (kg/cm ²)	Remarks
	Type	Content (weight %)	Type	Specific surface area (m ² /g)	Content (weight %)		
1	Apatite hydroxide	100	—	—	0	800	Out of claims
2	Apatite hydroxide	95	A	0.6	5	1450	Out of claims
3	Apatite hydroxide	95	A	2.5	5	2080	Within claims
4	Apatite hydroxide	95	A	4.5	5	2340	Within claims
5	Apatite hydroxide	95	B	0.6	5	1200	Out of claims
6	Apatite hydroxide	95	B	2.5	5	1810	Within claims
7	Apatite hydroxide	95	B	4.5	5	2000	Within claims
8	Calcium triphosphate	95	A	2.5	5	1750	Within claims
9	Mixture	95	A	2.5	5	1670	Within claims

Note) The sintered compact No. 1 was especially weak in spalling resistance.